# Quantum ordering of protons in cold solid hydrogen

M. A. Iontsev
*P.N. Lebedev Physical Institute of RAS, Moscow, Russia,*
*e-mail: mikhail.iontsev@gmail.ru*

A combination of state-of-the-art theoretical methods has been used to obtain an atomic-level picture of classical and quantum ordering of protons in cold high-pressure solid hydrogen. We focus mostly on phases II and III of hydrogen, exploring the effects of quantum nuclear motion on certain features of these phases (through a number of ab initio path integral molecular dynamics (PIMD) simulations at particular points on the phase diagram). We also examine the importance of van der Waals forces in this system by performing calculations using the optB88-vdW density functional, which accounts for non-local correlations.

Our calculations reveal that the transition between phases I and II is strongly quantum in nature, resulting from a competition between anisotropic inter-molecular interactions that restrict molecular rotation and thermal plus quantum fluctuations of the nuclear positions that facilitate it. The transition from phase II to III is more classical because quantum nuclear motion plays only a secondary role and the transition is determined primarily by the underlying potential energy surface.

A structure of P21/c symmetry with 24 atoms in the primitive unit cell is found to be stable when anharmonic quantum nuclear vibrational motion is included at finite temperatures using the PIMD method. This structure gives a good account of the infra-red and Raman vibron frequencies of phase II. We found additional support for a C2/c structure as a strong candidate for phase III, since it remained transparent up to 300 GPa, even when quantum nuclear effects were included. Finally, we found that accounting for van der Waals forces improved the agreement between experiment and theory for the parts of the phase diagram considered, when compared to previous work which employed the widely-used Perdew–Burke–Ernzerhof exchange–correlation functional.

**References**

1. H.K. Mao, R.J. Hemley. Rev. *Mod. Phys.* (1994) 66: 671.
2. J.M. McMahon, M.A. Morales, C. Pierleoni, D.M. Ceperley. *Rev. Mod. Phys.* (2012) 84: 1607.
3. M.I. Eremets, I.A. Troyan. Nature Mater. (2011) 10: 927.
4. R.T. Howie, C.L. Guillaume, T. Scheler, A.F. Goncharov, E. Gregoryanz. *Phys. Rev. Lett*. (2012) 108: 125501